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CHEMISTRY TECHNOLOGY:  
ADHESIVES AND PLASTICS

A COMPILATION



NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

# Foreword

The National Aeronautics and Space Administration has established a Technology Utilization Program for the dissemination of information on technological developments which have potential utility outside the aerospace community. By encouraging multiple application of the results of its research and development, NASA earns for the public an increased return on the investment in aerospace research and development programs.

This publication is part of a series intended to provide such technical information. The 30 items presented are divided into two sections. In section one, a group of chemical formulations having to do with the production or improvement of adhesives is listed. Section two treats of a group of polymeric plastics that feature special characteristics or that are produced by innovative methods.

Additional technical information on individual devices and techniques can be requested by circling the appropriate number on the Reader Service Card included in this compilation.

Unless otherwise stated, NASA contemplates no patent action on the technology described.

We appreciate comment by readers and welcome hearing about the relevance and utility of the information in this compilation.

Jeffrey T. Hamilton, *Director*  
*Technology Utilization Office*  
*National Aeronautics and Space Administration*

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# Contents

<b>SECTION 1. Chemistry Related To Adhesives</b>	<b>Page</b>
New Class of Thermosetting Plastics has Improved Strength, Thermal and Chemical Stability .....	1
Arylenesiloxane Copolymers .....	2
Photosensitive Filler Minimizes Internal Stresses in Epoxy Resins .....	2
Synthesis of Pure Aromatic Glycidyl Esters for Use as Adhesives .....	3
Nonflammable and Liquid Oxygen-Resistant Adhesives .....	3
High Temperature Bis (epoxyalkyl) Carborane Adhesives .....	4
Improved Synthesis of 1-Vinylnaphthalene .....	5
 <b>SECTION 2. Polymer Plastics</b>	
Silazane Polymers Show Promise for High Temperature Applications .....	6
Substituted Silane-Diol Polymers Have Improved Thermal Stability .....	7
Highly Fluorinated Polyurethanes .....	8
Silazane Elastomer Remains Resilient at 400°C .....	9
Process Produces Chlorinated Aromatic Isocyanate in High Yield .....	10
Synthesis of Various Highly Halogenated Monomers and Polymers .....	10
Treatment of Polymers with Iodine Reduces Static Electricity Problem .....	10
New Rapid-Curing, Stable Polyimide Polymers with Strength and Stability at High Temperatures .....	11
Reinforcement of Polymeric Structures with Asbestos Fibrils .....	12
Tensile Creep-Rate of Pyrolytic Carbon .....	14
Polymerization of Perfluorobutadiene .....	14
Polyimide Polymers Provide Improved Ablative Materials .....	15
Difunctional Polyisobutylene Prepared by Polymerization of Monomers on Molecular Sieve Catalyst .....	16
New Hyperthermal Thermosetting Heterocyclic Polymers .....	17
Process for Synthesizing a New Series of Fluorocarbon Polymers .....	17
Soluble, High Molecular Weight Polyimide Resins .....	18
Filled Polymers for Bearings and Seals Used in Liquid Hydrogen .....	19
Preparation of Perfluoropolyether Prepolymers .....	19
Polymer Containing Functional End Groups is Base for New Polymers .....	20
Polymerization of Perfluorobutadiene at Near-Ambient Conditions .....	20
Coatings from Copolymers of Tetraphenoxysilane and p,p'-Biphenol .....	21
Polyimide Polymers Provide Higher Char Yield for Graphitic Structures .....	21

# Section 1. Chemistry Related To Adhesives

## NEW CLASS OF THERMOSETTING PLASTICS HAS IMPROVED STRENGTH, THERMAL AND CHEMICAL STABILITY

A new class of thermosetting plastics, designated cyclized polydiene urethane resins, has been developed to have high hydrocarbon content, high strength modulus (stiffness), thermal stability, humidity resistance, and workability in the precured state. One series of these polydiene polymers is called cyclized polybutadiene urethane (HYSTL) resins which are rich in hydrocarbons and consist of molecular chains of cross-linked, condensed cyclohexane rings interconnected by urethane bonds.

Another series, called cyclized polyisoprene-urethanes, yields plastics consisting of molecular chains cross-linked, condensed methylcyclohexane rings interconnected by urethane bonds and thus are very similar to the cyclized polybutadiene-urethanes.

The polybutadiene resin is formed by reacting a long chain 1,2-polybutadiene diol with a diisocyanate at moderate temperatures and then initiation of the free radical induced cyclization of the pendant vinyl groups. The polyisoprene resin employs 3,4-polyisoprene diol in the reaction instead of the 1,2-polybutadiene diol. These cyclized polydiene-urethane resins have several unique features including: low density, high chemical resistance, easily processed, high thermal stability, resistance to water absorption, high resistance to UV exposure, high compressive strength, and high carbon content.

These polydiene-urethane polymer systems can be used as high temperature adhesives, matrices for reinforced structural plastics, and for the preparation of plastic parts which have chemical and moisture resistance and dimensional stability.

The reinforced structures prepared using these classes of resins exhibited high thermal, oxidative, hydrolytic, and chemical stability. Structural plastics

prepared using these resin systems show promise for use in ablative materials, deep submergence ocean vessels, and lightweight structural plastics. The use of cyclized polybutadiene urethane resin systems permits preparation of composite structures by vacuum bag lay-up methods, preimpregnation and pressing, tape winding and curling, and filament winding procedures. The reinforced structural plastic can be prepared without the elimination of volatile matter, thus permitting use of processing techniques which require relatively low mechanical pressures.

Both the polybutadiene and polyisoprene resins can be used as high temperature adhesives having thermal stability in excess of 400°C. These adhesives also exhibit excellent oxidation and chemical stability and can be applied at moderate temperatures to effect the adhesive bonding.

Polydiene-urethane resins can also be used as protective coatings, showing exceptional chemical resistance in particular. It is possible to apply the coating in the form of an aerosol, paint, and dip, either in a carrier or in the neat liquid uncured form. The protective coating is practically colorless, consequently, pigments of dyes can be formulated into the mixture to provide desirable colors.

Title to this invention has been waived under the provisions of the National Aeronautics and Space Act [42 U.S.C. 2457 (f)], to TRW Systems, One Space Park, Redondo Beach, California 90278.

Source: H. R. Lubowitz, E. A. Burns, and  
B. Dubrow of  
TRW Systems  
under contract to  
Lewis Research Center  
(LEW-10108)

### ARYLENESILOXANE COPOLYMERS

Arylenesiloxane copolymers, as a class, have been the subject of considerable investigation in efforts to develop organosilicon polymers (for use as adhesives, laminating resins, and coatings) having improved physical and chemical properties, including stability at elevated temperatures. These efforts have led to the preparation of new arylenesiloxane copolymers having regularly ordered structures.

The copolymers were typically prepared by heating different mixtures of arylenesilane and siloxazane monomers in a 25x140 mm polymerization tube immersed in a Wood's metal bath for a specified time (generally 8 hours) at 160°C. A number of copolymerizations were also carried out in solution.

Both the arylenesilane and siloxazane monomers, which were synthesized in these experiments, were either previously unknown compounds or had not been prepared in a sufficiently high degree of purity. The arylenesilanes consisted of the following compounds:

1. p-phenylenebis(dimethylsilanol);
2. m-phenylenebis(dimethylsilanol);

3. p-phenylenebis(methylphenylsilanol);
  4. m-phenylenebis(methylphenylsilanol);
  5. p-phenylenebis(diphenylsilanol);
  6. m-phenylenebis(diphenylsilanol);
  7. bis(p-dimethylhydroxysilylphenyl) ether; and
  8. bis(p-hydroxymethylphenylsilylphenyl) ether.
- The siloxazanes which were synthesized included the following compounds:
1. decamethyl-1, 5-diaza-3,5-dioxo-2,4,6,8-tetrasilacyclo-octane;
  2. heptamethyl-1-aza-3,5-dioxo-2,4,6-trisilacyclohexane; and
  3. nonamethyl-1-aza-3,5,7-trioxa-2,4,6,8-tetrasilacyclo-octane.

Source: L. W. Breed and R. L. Elliott of  
Midwest Research Institute  
under contract to  
Marshall Space Flight Center  
(MFS-1812)

*Circle 1 on Reader Service Card.*

### PHOTOSENSITIVE FILLER MINIMIZES INTERNAL STRESSES IN EPOXY RESINS

Addition of a photosensitive filler, such as cinnamic acid resins and cinnamal ketones, to a curable epoxy resin mixture, in the amount of 1% to 3% by weight of the resin mixture, relieves the internal stress that weakens such compounds during the cure cycle. Normal techniques to minimize detrimental high shrinkage include curing at relatively low temperatures and adding inert fillers to decrease the exothermic heat. These techniques have their inherent disadvantages which makes using them unsatisfactory.

The addition of the fillers before cure does not inhibit the curing or polymerization of the epoxy system since the volume of filler is minute. The resultant mixture is then cured in the conventional fashion, as by the addition of heat or a catalyst. After curing, the epoxy resin, if clear, displays internal isoclinic stress lines when viewed under polarized light. The epoxy resin is then exposed to a strong ultraviolet light source. Such exposure is for

a time sufficient to allow the photosensitive filler to polymerize and relieve the internal stresses. When the epoxy resin is again viewed under polarized light, it is observed that the internal stress lines have disappeared. This indicates an epoxy resin that has high resistance to thermal shock and conditioning.

This method to relieve internal stress eliminates the use of inert fillers. They frequently tend to settle out of solution before curing thus producing a nonuniform and weakened structural system. Inert fillers invariably lower the continuous service temperature or heat distortion point of an epoxy system.

Source: J. N. Dillon of  
IBM  
under contract to  
Marshall Space Flight Center  
(MFS-1880)

*Circle 2 on Reader Service Card.*

## SYNTHESIS OF PURE AROMATIC GLYCIDYL ESTERS FOR USE AS ADHESIVES

An extensive laboratory study was conducted to synthesize pure glycidyl esters of aromatic acids and to convert the resultant epoxy esters to polymers for use as adhesives over a range of temperatures down to 20.5 K ( $-423^{\circ}\text{F}$ ).

Diglycidyl phthalate and diglycidyl terephthalate, for example, have been prepared by other investigators from glycidol and the appropriate aromatic acid chlorides in the presence of the base, triethylamine. The disadvantage of the earlier procedure is that glycidol itself polymerizes exothermally in the presence of a base and thus forms a byproduct which contaminates the desired pure product. The improved procedure which has been developed involves low reaction temperatures and the addition of the acid chloride at a slightly faster rate than that of the triethylamine. Many of the pure crystalline products synthesized in this program have been reported by earlier investigators as resins.

The pure aromatic glycidyl esters were polymerized to high molecular weight materials by reacting them with amines and anhydrides. These polymers were then applied as adhesives to test panels and subjected to physical testing for adhesive strength over a

range of temperatures.

Several of the adhesives were found to meet most of the temperature requirements but did not have the proper T-peel strength when cured at 296 K ( $73^{\circ}\text{F}$ ). As the adhesives become more flexible to meet the T-peel requirements, the tensile shear strengths at 394 K and 478 K ( $250^{\circ}$  and  $400^{\circ}\text{F}$ ) begin to decrease. Consequently, it is not feasible to prepare adhesives meeting the tensile shear requirements and having a T-peel strength in excess of  $69 \times 10^3 \text{ N/m}^2$  (10 psi). It appears that curing at room temperature is sufficient for some of the epoxies where high tensile shear strength at 478 K ( $400^{\circ}\text{F}$ ) is not required. Curing at elevated temperatures produces a more cross-linked adhesive which shows greater rigidity and lower T-peel strength, but good tensile shear strength at the elevated temperatures.

Source: The Borden Chemical Co.  
under contract to  
Marshall Space Flight Center  
(MFS-12705)

*Circle 3 on Reader Service Card.*

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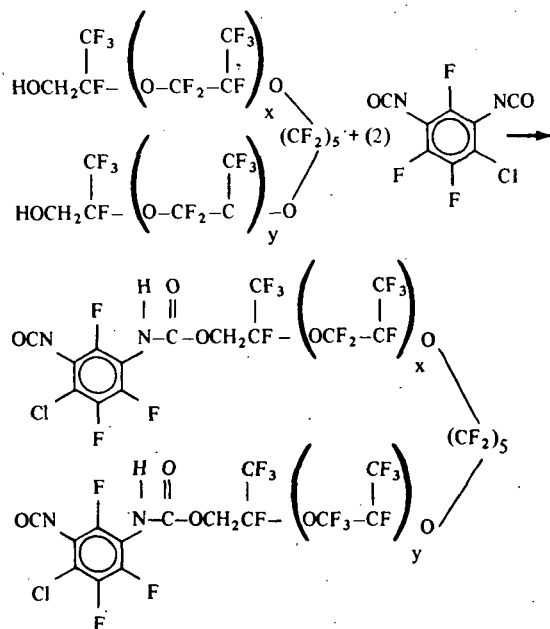
## NONFLAMMABLE AND LIQUID OXYGEN-RESISTANT ADHESIVES

A two-component adhesive system has been prepared, based on highly fluorinated polyurethanes, from hydroxyl-terminated highly fluorinated polyethers. The polyethers used are more thermally and chemically resistant than conventional polyethers, resulting in an adhesive system which is nonflammable in oxygen and resistant to impact in LOX. Furthermore, they were found to be resistant to strong oxidizers such as  $\text{N}_2\text{O}_4$ .

### Preparation:

An isocyanate-terminated prepolymer is prepared from a hydroxyl-terminated polyether of perfluoropropylene oxide as follows:

The hydroxyl-terminated fluorinated polyether of 1700 molecular weight (25.5 g, 0.015 mole) and 1-chloro-2,4-diisocyanate-3,5,6-trifluorobenzene (7.47 g, 0.30 mole) is heated at  $60^{\circ}$ - $80^{\circ}\text{C}$  for 1/2 hour, followed by 1 hour and 40 minutes at  $80^{\circ}$ - $100^{\circ}\text{C}$ . The reaction is as follows:



Based on the infrared spectra, the reaction was complete. It was then cooled to 80°C, and 1-chloro-2,4-diisocyanate-3,5,6-trifluorobenzene (3.73 g, 0.015 mole) was added. It was then cooled to room temperature (RT). This material is designated Component A.

The adhesive is prepared by combining 15 parts of Component A with the hydroxyl-terminated fluorinated polyether of 1700 molecular weight (7.05 g) and 0.3 g of iron naphthenate catalyst. This is 1.8 equivalents of NCO to 1.0 of OH. Coupons of 2024-T3 aluminum were bonded with this adhesive and cured overnight in a vacuum bag at RT, followed by a postcure of 48 hours at 344 K (160°F). The adhesive had a tensile shear of  $373 \times 10^5 \text{ N/m}^2$

(5400 psi) at 78 K (−320°F) and  $97 \times 10^5 \text{ N/m}^2$  (1400 psi) at RT.

The isocyanate-terminated prepolymer described above is preferred and was prepared to reduce any possible toxicity problem with using all diisocyanate. However, a prepolymer need not be prepared. For example, an adhesive was prepared by mixing the hydroxyl-terminated fluorinated polyether of 1600 molecular weight (7.3 g, 0.0045 mole) with 1-chloro-2,4-diisocyanate-3,5,6-trifluorobenzene (2.01 g, 0.0081 mole) and 1 drop of stannous octoate catalyst. Bonds were prepared as described previously. The tensile shear strength of the material was  $124 \times 10^5 \text{ N/m}^2$  (1800 psi) at RT and  $317 \times 10^5 \text{ N/m}^2$  (4600 psi) at 78 K (−320°F).

Other halogenated diisocyanates such as tetrafluoro-m-phenylene diisocyanate, tetrafluoro-p-phenylene diisocyanate, etc. can be used. For example, an adhesive was prepared using tetrafluoro-m-phenylene diisocyanate in place of 1-chloro-2,4-diisocyanate-3,5,6-trifluorobenzene. The bond strengths on aluminum was  $138 \times 10^5 \text{ N/m}^2$  (2000 psi) at RT and  $324 \times 10^5 \text{ N/m}^2$  (4700 psi) at 78 K (−320°F).

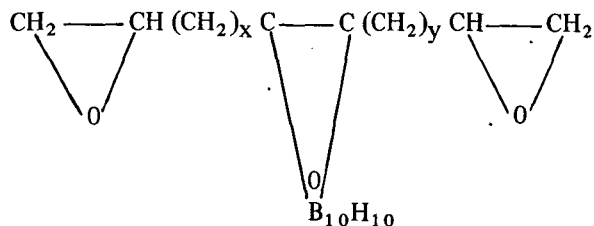
The adhesive is usable over the range of 78 K (−320°F) to 367 K (200°F), or for very short exposures to 394 K (250°F). Fillers or additives may be added to the adhesive system to impart particular properties. However, these are not required.

Source: F. D. Trischler and J. Hollander of Whittaker Corp. under contract to Marshall Space Flight Center (MFS-20392)

Circle 4 on Reader Service Card.

## HIGH TEMPERATURE BIS (EPOXYALKYL) CARBORANE ADHESIVES

A group of bis (epoxyalkyl) carborane monomers have been prepared and polymerized for use as high temperature adhesives. The bis (epoxyalkyl) carboranes involved have the following composition:

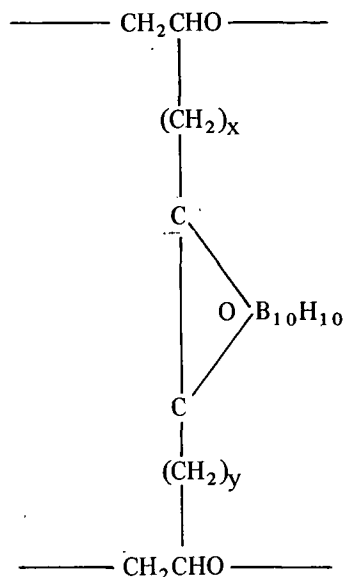


The following bis (epoxyalkyl) carboranes have been prepared and characterized:

1.  $x=y=2$ , Bis (epoxybutyl) carborane, melting point 68-71°C,
2.  $x=y=3$ , Bis (epoxypentyl) carborane, melting point 68-75°C,
3.  $x=y=4$ , Bis (epoxyhexyl) carborane, room temperature liquid.

These epoxies can be cured to hard solids by conventional curing catalysts and reactive hardeners.

The polyether formed by the action of a catalyst would have the following structure:



The epoxy monomers can be B-staged and cured under a variety of conditions. For example, with the catalyst boron trifluoride: monoethylamine, the bis (epoxyalkyl) carboranes can be B-staged to produce nonflowing plastics having string-forming characteristics at room temperature. Excellent bonding of 17/7 stainless steel is obtained when the epoxies are cured at temperatures slightly above 100°C under moderate pressure. Representative lap-shear strengths, when catalyzed with 3%  $\text{BF}_3 \cdot \text{EtNH}_2$  are as follows:

#### Adhesive

#### Lap-Shear Strength

Bis (epoxybutyl) carborane  $160 \times 10^5 \text{ N/m}^2$  (2320 psi)  
 Bis (epoxypentyl) carborane  $194 \times 10^5 \text{ N/m}^2$  (2810 psi)  
 Bis (epoxyhexyl) carborane  $248 \times 10^5 \text{ N/m}^2$  (3600 psi)

Lap-shear strengths as high as  $67 \times 10^5 \text{ N/m}^2$  (980 psi) have been obtained at 478 K (400°F) in an air atmosphere with the bis (epoxybutyl) carborane/3%  $\text{BF}_3 \cdot \text{EtNH}_2$  catalyst system.

Superior high temperature performance is obtained with a reactive curing agent. Lap-shear strength as high as  $121 \times 10^5 \text{ N/m}^2$  (1770 psi) has been obtained at 533 K (500°F) in an air atmosphere with bis (epoxybutyl) carborane cured with 4,4'-diaminodiphenylsulfone. These values, which represent 80% retention of room temperature strength,  $152 \times 10^5 \text{ N/m}^2$  (2200 psi), were obtained from samples which had been previously soaked at 533 K (500°F) for two hours. At 478 K (400°F), 100% of room temperature lap-shear strength is retained. Strengths as high as  $101 \times 10^5 \text{ N/m}^2$  (1460 psi) at 533 K (500°F) in an air atmosphere have been obtained on samples soaked at 533 K (500°F) for 24 hours.

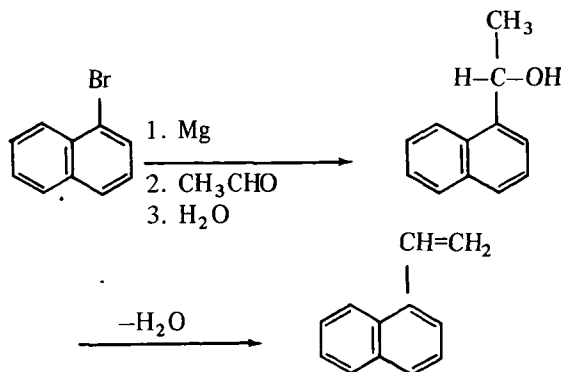
Title to this invention has been waived under the provisions of the National Aeronautics and Space Act [42 U.S.C. 2457 (f)], to General Precision Systems, Inc., Kearfott Group, 1150 McBride Ave., Little Falls, N. J. 07424.

Source: R. Barnes and D. Grafstein of  
 General Precision Systems, Inc.  
 under contract to  
 Manned Spacecraft Center  
 (MSC-12207)

## IMPROVED SYNTHESIS OF 1-VINYLNAPHTHALENE

A procedure for preparation of 1-Vinylnaphthalene has proven superior to previous methods in that it results in reproducible yields of 43% for the first step and 90% for the second step. According to the literature, previous yields have not exceeded 80%.

1-vinylnaphthalene is usually prepared by the following reaction sequence:





In this procedure magnesium turnings (24.3 g, 1 mole) are placed in a 2-liter 3-neck flask equipped with a mechanical stirrer, a reflux condenser, and a 1-liter addition funnel. A nitrogen atmosphere is maintained in the flask. After the entire apparatus is flamed, 207 g (1 mole) of freshly distilled 1-bromonaphthalene (Eastman Kodak, b.p. 100°C, 1 torr) and 500 ml of dried tetrahydrofuran are placed in the addition funnel and a small portion added to the stirred magnesium turnings. The mixture is stirred and heated gently until the reaction begins. The remaining solution is then added slowly so as to maintain gentle reflux. On completion of this reaction, 44 g (1 mole) of acetaldehyde (Eastman Kodak, used as received) dissolved in 300 ml of tetrahydrofuran is slowly added from the addition funnel.

Next, 150 g of ammonium chloride in 500 ml of water is added with rapid stirring, the mixture transferred to a separatory funnel, and the aqueous layer separated. After washing twice with tetrahydrofuran, the combined extracts and the original organic layer are combined and the tetrahydrofuran removed by distillation. The remaining brown solid is refluxed with 750 ml of petroleum ether (65-110°C) and the cooled solution filtered and washed twice with 50 ml of petroleum ether, 72.0 g (41.9%) m.p. 65°C.

The dehydration is performed as follows: a 60.9 cm (2-ft)-long, 2.54 cm (1 in)-diameter Pyrex column provided with a thermocouple well is packed to a depth of 35.6 cm (14 inches) with 4-mesh Alcoa activated alumina and topped with a 2.54 cm (1 inch)-height of glass beads. A dropping funnel containing the carbinol is placed on top of the column and a receiving flask cooled to -76°C at the bottom. A 0.5-torr vacuum is established; the column is heated to 300°C, and the carbinol is melted in the dropping funnel by means of an infrared lamp and allowed to degass for one hour. Next the molten carbinol is slowly allowed to drop through the column and the product collected in the receiving flask. The yield of 1-vinylnaphthalene is usually of the order of 90%.

The improvement for the first step consists of using tetrahydrofuran as solvent instead of diethyl ether. Although this does not result in improved yields the ease of the reaction is considerably enhanced.

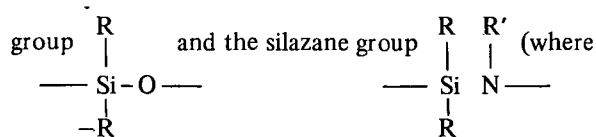
Source: J. Heller and D. B. Miller of  
Stanford Research Institute  
under contract to  
NASA Pasadena Office  
(NPO-10551)

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## Section 2. Polymer Plastics

### SILAZANE POLYMERS SHOW PROMISE FOR HIGH TEMPERATURE APPLICATIONS

Polymers are needed that will be useful as adhesives, structural plastics, elastomers, and laminating resins in extreme environments. Certain chemical (isoelectronic and isosteric) similarities between the silicone



R and R' are organic radicals) have suggested that, with the proper substituents on the silicon and nitrogen atoms, it should be possible to develop silazane polymers having a useful temperature range beyond that of the silicones.

A number of intermediate compounds and polymers containing silicon-nitrogen bonds show promise as high temperature coatings and elastomers that exhibit stability to temperatures in the range of 300° to 400°C.

Several silazane polymers were prepared by reacting dimethyldichlorosilane  $[(\text{CH}_3)_2\text{SiCl}_2]$  with various organic diamines  $[\text{R}(\text{NH}_2)_2]$ . The diamines used included ethylenediamine; 1,3-propanediamine; 1,6-hexanediamine; 1,4-phenylenediamine; piperazine; benzidine; and 4,4' methylenedianiline.

A one-step reaction involving a 1:1:2 molar ratio of dimethyldichlorosilane, ethylenediamine, and triethylamine as an acid acceptor produced a poly-ethylenediaminesilazane. The reaction was conducted

in a one liter, three-neck flask equipped with a stirrer, dropping funnel, and reflux condenser. To this flask was added a solution of 0.2 mol of dimethyldichlorosilane in 200 ml of dry benzene. A separate solution containing 0.2 mol of ethylenediamine and 0.4 mol of triethylamine in 100 ml of dry benzene was then added dropwise, with constant stirring, over a 90-minute period. The resulting solution was then refluxed for 3.5 hours. At the end of this time, the triethylamine hydrochloride produced in the reaction was filtered off, and the benzene was evaporated under reduced pressure. The product, containing approximately 67% solids, was applied to an aluminum plate; the excess solvent was removed by heating at 70°C for 18 hours, and the resulting film was cured at 204°C for 2 hours and then at 315°C for 1 hour. The transparent, smooth, elastomeric film could be peeled from the plate, but has relatively low strength. It remained unchanged in physical appearance and retained its elasticity after standing for 17 months under normal atmospheric conditions.

The silazanes prepared by reacting dimethyldichlorosilane with the other diamines yielded foamed elastomers, rigid foamed solids, powders, waxes, and viscous liquids of varying properties.

An analogous series of polymers, prepared by reacting diphenyldichlorosilane  $[(C_6H_5)_2SiCl_2]$  with four different organic diamines, in the manner described above, yielded polymers ranging from tacky gels to brittle solids. When cured at 400°C, some of these materials formed stable polymers.

Several potentially useful polymers were prepared by chain-opening reactions between equimolar amounts of hexaphenylcyclotrisilazane and various diols. Some of these materials exhibited good film and fiber forming properties. One of these materials is stable at temperatures up to 500°C.

The following documentation may be obtained from:

National Technical Information Service  
Springfield, Virginia 22151  
Single document price \$6.00  
(or microfiche \$0.95)

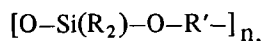
#### Reference:

NASA SP-5030 (N66-17706) Symposium on Technology Status and Trends.

Source: J. D. Byrd and J. E. Curry  
Marshall Space Flight Center  
(MFS-466)

## SUBSTITUTED SILANE-DIOL POLYMERS HAVE IMPROVED THERMAL STABILITY

In order to synthesize a series of organosilicon polymers with improved physical and chemical properties, including stability at elevated temperatures, a series of polymers of the general formula



where R represents an aryl group, and R' represents an alkyl, aryl-substituted alkyl, biphenyl or diphenyl ether group, have been investigated.

The experimental work was confined to the polymerization of the stable silylamine, bis (anilino) diphenylsilane  $(C_6H_5)_2Si(NHC_6H_5)_2$ , with various diols, including hydroquinone; resorcinol; p,p'-biphenol; 2,7-naphthalenediol; 2,2-propane-bis-(4-hydroxybenzene); 1,6-hexanediol; and 4,4'-dihydroxy diphenyl ether. The silylamine was prepared by reacting diphenyldichlorosilane and aniline. The diols, obtained from commercial sources, were recrystallized before use.

In conducting a polymerization, equimolecular amounts of the silylamine and the selected diol were placed in a thick-walled resin kettle fitted with a heating mantle to facilitate removal of the aniline produced in the reaction, a takeoff condenser, and a vacuum line. A hotplate-magnetic stirrer combination was used for heating and mixing the reactants. Approximately 30 minutes after the reactants were melted, the pressure in the kettle was slowly reduced to approximately 1 mm of Hg, and the reaction was allowed to proceed at a temperature of 300° to 325°C for approximately 6 hours. The polymer produced in the reaction was then removed from the kettle and subjected to various chemical and physical tests.

Of the several polymers that were produced, poly (4,4'-bisoxypiphenylene) diphenylsilane  $[-Si(C_6H_5)_2-O-C_6H_4-C_6H_4-O-]_n$ , formed from bis (anilino) diphenylsilane and p,p'-biphenol, was found to have the most desirable properties. The bulk polymer is a

hard, slightly brittle, amber colored solid. It forms a hard protective coating on aluminum, remains stable after being heated at 500°C for 60 minutes, and shows no change after 96 hours at 270°C. The polymer also forms transparent, semi-flexible films and appears to be suitable for use as an adhesive.

The application of the poly (4-4'-bisoxybipheny-

lene) diphenylsilane as a thermal-control coating appears to be especially promising.

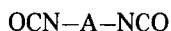
Source: J. E. Curry and J. D. Byrd  
Marshall Space Flight Center  
(MFS-469)


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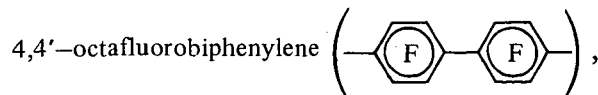
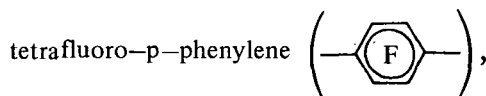
## HIGHLY FLUORINATED POLYURETHANES

New highly fluorinated polyurethanes are prepared either by reaction of fluorinated diisocyanates, haloformates with fluorinated or non-fluorinated diols, or by reaction of fluorinated bis-haloformates with fluorinated diamines. These polyurethanes possess improved flame resistance and improved chemical resistance.

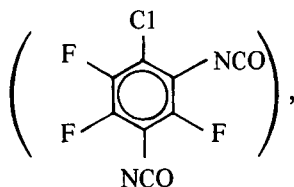
The polymers are prepared by reaction of a fluorinated diisocyanate having the following formula:



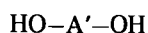
wherein A is tetrafluoro-m-phenylene ,

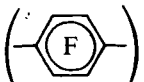


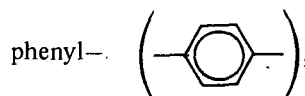
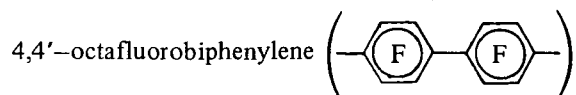
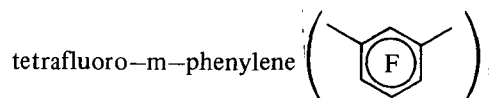
1-chloro-3,5,6-trifluoro-2,4-phenylene



hexafluoropentamethylene  $[-\text{CH}_2(\text{CF}_2)_3\text{CH}_2-]$ , or perfluorotrimethylene  $(-\text{CF}_2\text{CF}_2\text{CF}_2-)$  with a diol having the formula:



wherein A' is tetrafluoro-p-phenylene ,

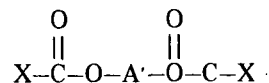


hexafluoropentamethylene  $[-\text{CH}_2(\text{CF}_2)_3\text{CH}_2-]$ , and pentamethylene  $[-(\text{CH}_2)_5-]$ .

Alternately, these polymers may be prepared by reaction of a fluorinated diamine having the following formula:



with a fluorinated or nonfluorinated bis-haloformate having the formula:



wherein A and A' are as defined above and X is a halogen such as fluorine, chlorine, bromine, or iodine.

One example that produced excellent high temperature polyurethane is poly (pentamethylene tetrafluoro-p-phenylene dicarbamate). It was prepared in the following manner.

A solution of 1,5-pentanediol (2.1 g, 0.02 mole) dissolved in 10 ml of ethyl acetate was placed in a 100-ml, three-necked flask equipped with a stirrer, reflux condenser, and addition funnel with a nitrogen inlet. The system was flushed with nitrogen

and the polymerization run under a nitrogen atmosphere. Tetrafluoro-*p*-phenylene diisocyanate (4.6 g, 0.02 mole) dissolved in 15 ml of ethyl acetate was added slowly with stirring over a period of 25 minutes. Almost immediately, a white precipitate came out of solution. The mixture was stirred at room temperature for 1-1/2 hours, then at reflux (77°C) for 2-1/2 hours. The white solid was filtered and dried in a vacuum oven at 70°C yielding 6.1 g

(91%) of polyurethane melting at 280° to 281°C.

Source: F. D. Trischler, J. Hollander, and R. B. Gosnell of Whittaker Corp. under contract to Marshall Space Flight Center (MFS-14963)

*Circle 7 on Reader Service Card.*

## SILAZANE ELASTOMER REMAINS RESILIENT AT 400°C

In recent studies it has been found that a smooth, unfoamed elastomer in thicknesses of up to 1 millimeter can be obtained by heating mixtures of approximately 90 parts by weight of methylphenylsilazane with only 10 parts by weight of ethylenediamine silazane at 190°C for 18 hours in air. The elastomer is unaffected by common acids, alkalis, and organic solvents. Its thermal stability, chemical resistance, and physical properties should make it of interest for various applications. The methods of preparing the reactants and the elastomer product are described below.

### Preparation of "methylphenylsilazane".

In a 2-liter, 3-neck flask fitted with a stirrer, reflux condenser, thermometer, and gas inlet tube, were placed 1600 ml of dry benzene and 191.1 g (1.0 mole) of methylphenyldichlorosilane. Ammonia, previously dried over sodium, was passed over the liquid, with constant stirring for 3 hours; and the resulting mixture was refluxed for 3 hours. The clear supernatant liquid was negative to the Beilstein test for halogens. The residue was filtered off and extracted with benzene, and the product was isolated by distilling off the benzene, finally, at reduced pressure. The pot temperature did not exceed 80°C. The product, called "methylphenylsilazane," was a cloudy, viscous liquid weighing 129.2 g.

On heating the product, the results were similar to those obtained with a variety of silazanes in that fibers could be pulled from the melt, but which were

not tough polymers with high softening points. Continued heating produced foamed solids with high chemical and thermal stability.

### Preparation of an elastomer from the "methylphenylsilazane" and ethylenediamine silazane.

The "methylphenylsilazane" was partially polymerized by boiling it in a test tube for 3 minutes. When cool, it was mixed with 10 percent by weight of ethylenediamine silazane (prepared by the method described in Tech Brief 66-10194), and the mixture was heated in an oven at 190°C for 18 hours. A non-foamed elastomer was produced in a maximum thickness of 1 mm.

The elastomer was unaffected by acetone, tetrahydrofuran, acids, and alkalis, and was unchanged after being heated at 190°C for 8 days. The sample retained most of its original resilience after being heated at 400°C for 2 hours. No simple formula can now be proposed for the elastomer.

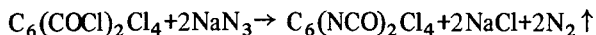
A sample of glass cloth coated with the elastomer formed a flexible, impervious sheet. This composite should be useful as a gasketing material for application at higher temperatures (up to 400°C).

Source: Southern Research Institute under contract to Marshall Space Flight Center (MFS-1144)

*Circle 8 on Reader Service Card.*

## PROCESS PRODUCES CHLORINATED AROMATIC ISOCYANATE IN HIGH YIELD

This method prepares tetrachloro-p-phenylene diisocyanate in high yield. The diisocyanate is prepared by reacting tetrachloroterephthaloyl chloride with sodium azide (in an atmosphere of nitrogen) in accordance with the following equation:



A slurry of sodium azide (1.2 mole) in dry xylene (600 ml) is placed into a three-necked, two-liter flask equipped with a stirrer, thermometer, condenser, dropping funnel, and nitrogen inlet. A solution of tetrachloroterephthaloyl chloride (0.3 mole) in dry xylene (600 ml) is then slowly (over a 45-minute period) mixed into the contents of the flask, maintained under a nitrogen atmosphere. The reaction (with constant stirring of the contents in the flask under nitrogen) is allowed to proceed at 135°C for

approximately 15 hours. The resultant slurry is cooled and filtered, and the xylene is evaporated from the filtrate, leaving a residue of approximately 96 percent-pure tetrachloro-p-phenylene diisocyanate in 96.8 percent yield.

The chlorinated diisocyanate should have application as an intermediate in the preparation of polyurethane foams; the high halogen content would impart added flame resistance to these foams.

Title to this invention has been waived under the provisions of the National Aeronautics and Space Act [42 U.S.C. 2457 (f)], to the Whittaker Corp., 3540 Aero Court, San Diego, California 92123.

Source: F. Trischler of  
Whittaker Corp.  
under contract to  
Marshall Space Flight Center  
(MFS-1658)

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## SYNTHESIS OF VARIOUS HIGHLY HALOGENATED MONOMERS AND POLYMERS

Sixteen new highly halogenated polyurethanes and one new highly halogenated polycarbonate have been prepared. These polymers were tested for liquid oxygen (LOX) compatibility. The results indicate that if the nitrogen is attached to a difluoromethylene, a tetrafluoro-p-phenylene, or a tetrachloro-p-phenylene group, urethane linkages flanked on the alcohol side by a 1,1-dihydroperfluoroalkyl chain are stable to impact in LOX. The results also indicate that urethane, amide, and ester groups do not, in themselves, impart LOX incompatibility. Polyurethanes prepared from hexafluoropentenediol were LOX compatible, but those prepared from certain modified

diols were LOX incompatible.

A number of other halogenated polymers such as halogenated polyamides, polyimides, polyureas, and halogenated polysulfite have been synthesized.

A related synthesis is described in NASA Tech Brief 66-10646 December, 1966.

Source: F. D. Trischler and J. Hollander of  
Whittaker Corp.  
under contract to  
Marshall Space Flight Center  
(MFS-2143)

*Circle 9 on Reader Service Card.*

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## TREATMENT OF POLYMERS WITH IODINE REDUCES STATIC ELECTRICITY PROBLEM

Unmodified organic polymers, as a class, show a very low degree of conductivity and permit a buildup of static electricity when near certain types of

electrical equipment. Known modified polymers are expensive to fabricate because they require fillers or bound metal salts.

One solution to the problem is to treat the organic polymers with iodine. Using a simple diffusion process, products of desired properties may be custom formulated because in many cases product properties are uniformly predictable.

This concept of increased conductivity by iodine modification has been substantiated by laboratory studies of films of poly-N-vinylcarbazole.

Poly-N-vinylcarbazole was precipitated twice from benzene and methanol and dried in a vacuum oven at 50°C. The high molecular weight polymer was dissolved in spectroscopic grade dichloromethane solvent. Iodine was then added to the solution, and the solvent removed at 0°C under vacuum in a rotating flask. The diffusion of iodine vapor into commercial polymeric films is an alternative and convenient

technique.

Commercial structural plastics, rubbers, and fibers resistant to static electricity effects are required for a wide variety of explosion-prone environments and working zones such as, for example, a naphtha dry cleaning plant. Utility is also foreseen in the medical field where surgical instruments and garments are used in the presence of explosive anesthetic vapors.

Source: A. Rembaum, A. M. Hermann, and  
R. F. Landel of  
Caltech/JPL  
under contract to  
NASA Pasadena Office  
(NPO-10062)

*Circle 10 on Reader Service Card.*

### NEW RAPID-CURING, STABLE POLYIMIDE POLYMERS WITH STRENGTH AND STABILITY AT HIGH TEMPERATURES

Polyimide resins are noted for their high temperature thermal stability and high temperature strength. Polyimides, thus, have found numerous applications in fields of advancing technology. While these outstanding high temperature properties make the polyimides attractive for many applications, processing problems have limited their full technical and economic potential.

Normally, polyimides are produced by the reaction between a dianhydride and a diamine. Reaction of the starting constituents at low temperature produces high molecular weight polyamic-acid by chain extension or polymerization requiring a period of 30 minutes for some varieties to as much as 4 hours for others. When this polyamic-acid formation has been completed, the material must be kept in solution, hermetically sealed and refrigerated if application is not anticipated within a few hours, to prevent hydrolytic degradation. Thus special packaging for subsequent storage is an expense which is passed on to the users. In the final product form, the polyamic-acid must be cured by heat treatment for a period of 5 to 16 hours at elevated temperatures to produce the polyimide, which process is accompanied by the evolution of an appreciable amount of volatile matter.

The problems of processing thermally stable polymer systems arise principally from the nature of the

condensation polymerization reaction. The solution to this difficulty lies in preparing thermally stable polymer precursors which polymerize by an addition-type reaction, thereby eliminating the volatile matter attendant with the condensation reaction.

A new addition-type polymerization reaction has been discovered, which is suitable for forming thermally stable polyimide polymers, and is based on utilization of reactive alicyclic rings positioned on the ends of polyimide prepolymers having relatively low molecular weights (1000-2000).

Reinforced structural plastics can be made by impregnating sheets of fibrous materials (glass, graphite, metals, cloth fabrics) with suspensions of these polyimide prepolymers. Amic acid precursors are prepared which are soluble in common laminating solvents. Reinforcement materials are impregnated with this varnish, and, following removal of excess solvent, the amic acid groups are converted to imide groups. The fully imidized prepolymer is stable for long durations at ambient conditions without special handling or storage requirements. Subsequently, the impregnated reinforcement is stacked and molded together at 589 K (600°F) and modest pressure  $69 \times 10^4 \text{ N/m}^2$ – $138 \times 10^4 \text{ N/m}^2$  (100–200 psi) and time (30-60 Minutes), depending on specimen thickness. Under these conditions, the reactive alicyclic rings at the terminal positions of the pre-

polymer coreact, causing resin flow, chain extension, and cross-linking to form a coherent, compact, high molecular weight, thermally stable polyimide-reinforced structure. This basic polymer system, called A-type polyimide, has been designed to (1) cure with the evolution of minimal volatile matter; (2) form from precursors that are oxidatively, thermally, and hydrolytically stable, and (3) require no post cure.

As a varnish, the A-type polyimide resin system permits processing by two different means; either using dry, tack-free, fully imidized prepregs, or tacky, partially advanced prepregs which have drape. The first approach provides a process which has essentially no volatile matter evolving during cure, and requires relatively short processing time. The second approach provides a prepreg which is easier to lay-up but requires a separate imidization step prior to molding to insure low void products. In either case, the polyimide differs from conventional commercial polyimide resin systems in that initially, imidization is performed on relatively low molecular weight prepolymers, while during final molding at 589 K (600°F), the chains extend and cross-link by a pyrolytic polymerization addition-type reaction that simultaneously fuses the plies together to form a coherent, compact, void-free product.

Specific applications of this resin system include ablative materials, supersonic aircraft structures, jet engine components, circuit boards, high temperature structures, flexible electrical cable insulation, and adhesive formulations.

Plastic molding powders with or without fillers or reinforcers can be prepared from these polyimide prepolymers. Molded items prepared from this class of resin show promise for use in ablative and high temperature applications, cryogenic applications, and as a self-lubricating bearing material. Items, such as seals, bearings, valve seats, and bushings, can be prepared by standard methods of compression and transfer moldings.

Title to this invention has been waived under the provisions of the National Aeronautics and Space Act [42 U.S.C. 2457 (f)], to TRW Inc., One Space Park, Redondo Beach, California 90278 (Attention: Mr. Ernest R. Boller).

Source: H. R. Lubowitz, J. F. Jones,  
E. A. Burns, W. R. Kendrick,  
R. S. Thorpe, and E. R. Wilson of  
TRW Inc.  
under contract to  
Lewis Research Center  
(LEW-10576)

## REINFORCEMENT OF POLYMERIC STRUCTURES WITH ASBESTOS FIBRILS

An experimental investigation was conducted to determine the structural potential of chrysotile asbestos fibrils, which have found wide use as reinforcements in various plastic matrixes; and to develop methods for dispersing macrofibers of the asbestos into colloidal-sized (200 to 500 Å) ultimate fibrils (abbreviated UAF) and for incorporating the UAF in matrixes without causing reagglomeration. Attempts to develop methods for producing UAF were undertaken because it was found that the tensile strength of conventional macroscopic asbestos fibers (abbreviated MF) increases as fiber diameter decreases. Fine-diameter MF, in the range of 10 to 20  $\mu$  ( $10^5$  to  $2 \times 10^5$  Å), have tensile strengths which have been reported to be as high as  $569 \times 10^7$  N/m<sup>2</sup> (824,000 psi) (U.S. Pat. 2,625,213). It is therefore reasonable to assume that 0.02  $\mu$  (200 Å) UAF could have strengths greater than  $690 \times 10^7$  N/m<sup>2</sup> (1,000,000

psi). A commercial method of producing asbestos fibrils (based on U.S. Pat. 2,626,213) for use as reinforcements in plastics composites yields a mixture of UAF and MF. In that method, the UAF-MF fibrils are produced by slow-speed stirring of a suspension of MF in a water solution of a suitable surfactant.

One of the results of the investigation was the development of an improved method for producing colloidal dispersions of asbestos in a water solution of any one of several commercially available surfactants (phosphate esters, for example). In this method, 100% UAF dispersions are obtained by high-speed shear-mixing of AY grade asbestos in aqueous surfactant solutions (in a commercial household blender, for example) for about 1-½ hours. The recovery of UAF, or UAF-MF, from the dispersing medium is accomplished by either of two

techniques. In the first technique, the dispersion is filtered to remove the larger fibers, and the filtrate containing the colloidal UAF is coagulated by adding water (or alcohol). The supernatant water is removed by filtration and the resultant mat or paper of UAF is dried. These papers were found to contain a high percentage of adsorbed surfactant. In the second technique, the UAF is recovered by evaporation of the water. In this case, the percentage of surfactant retained by the UAF is recovered by evaporation of the water. Thus, the percentage of surfactant retained by the UAF is recovered by evaporation of the water. Therefore, the percentage of surfactant retained by the UAF is even higher. To provide for the preparation of solid, void-free composites of high densities, the dried paper obtained by either technique is pressed at  $27.6$  to  $69 \times 10^5 \text{ N/m}^2$  (400 to 1000 psi). The densified paper may then be vacuum-impregnated with any one of a variety of resins. It was found that the surfactant adsorbed on the asbestos fibrils affects the ultimate bonding of the asbestos to the matrix in the composites prepared. In general, high proportions of residual surfactant tend to reduce the strength of asbestos/phenolic and asbestos/polyester composites. The papers containing 33% or more surfactant are remarkably strong (tensile strengths range from  $57 \times 10^5$  to  $421 \times 10^5 \text{ N/m}^2$  (820 to 6100 psi)) compared to papers with lower surfactant content (tensile strength of approximately  $6.9 \times 10^5 \text{ N/m}^2$  (100 psi)), before phenolic resin impregnation. In these papers, the surfactant may be acting as a lubricant, preventing the asbestos fibrils from cutting each other when placed under tension. When these papers containing 33% surfactant are impregnated with phenolic resin, the tensile strengths range from 317 to  $359 \times 10^5 \text{ N/m}^2$  (4600 to 5200 psi), depending on the composition of the surfactant used. However, the surfactant apparently interferes with resin/asbestos bonding. As expected, by orienting the asbestos reinforcement, an increase in strength (over isotropic reinforcement) was obtained in the direction of orientation. Partially oriented arrays of UAF were prepared by slowly drawing filaments of UAF from a water-diluted dispersion of UAF in an aqueous surfactant solution. When impregnated with phenolic resin, the arrays had tensile strengths up to  $6900 \times 10^5 \text{ N/m}^2$  (100,000 psi). UAF was thus found to be at least as strong as MF, although

anticipated strength advantage over MF was not demonstrated.

In the second and improved method, the UAF dispersions are prepared simply by mixing macro-sized asbestos fibers with any one of several organic liquids in the same type of high-speed blender used for the water-surfactant dispersions. The following are among the organic liquids which were found to serve as effective dispersants for the asbestos: ethylene glycol, mono-, di-, and tri-ethanolamine, glycerol, polyethylene glycol, polypropylene glycol, undecylenic acid, lauric diethanolamide, mineral oil, and linoleic acid. This method of producing UAF offers the following advantages:

- (1) The colloidal asbestos fibrils can be readily recovered free of adsorbed contaminants by evaporation of volatile dispersing media.
- (2) Selected dispersing liquids can serve as solvents for a matrix resin, thus allowing intimate mixing of the resin with UAF in the stage before the solvent is removed to produce an asbestos-reinforced resin.
- (3) Certain dispersing liquids can serve either as precursors of a matrix resin or as one of the components of a matrix resin, thus obviating the need to evaporate a solvent.

This method of producing colloidal asbestos dispersions in organic media should be particularly useful in the preparation of asbestos-reinforced plastics and elastomers; special lubricants; solvent-carried paints, varnishes, and adhesives; and in paper, film, and foil coatings where the fibrils must be free of surface contaminants.

The following documentation may be obtained from:

National Technical Information Service  
Springfield, Virginia 22151  
Single document price \$6.00  
(or microfiche \$0.95)

#### Reference:

- NASA-CR-893 (N67-36014), Colloidal Asbestos Fibrils as Reinforcements for Polymeric Structures  
NASA-CR-77225 (N67-34670), The Reinforcement of Polymeric Structures by Asbestos Fibrils  
Source: A. M. Schwartz and C. A. Rader of  
Harris Research Laboratories, Inc.  
under contract to  
NASA Headquarters  
(HQN-09954 and 09955)



## TENSILE CREEP-RATE OF PYROLYTIC CARBON

Pyrolytic carbon, also called pyrolytic graphite, has high strength at high temperature and is of considerable interest to industry. This material is deposited from thermally decomposed methane on a hot substrate at 2173 to 2573 K (1900-2300°C) in a very pure form having near-theoretical density with layer planes approximately parallel to the substrate. Although the as-deposited structure has disordered layer stacking, it graphitizes quite completely under the influence of high-temperature thermal and mechanical treatment. Pyrolytic carbon in fundamental studies serves as a model material representative of the broad class of graphitizing carbons and graphites.

The parallel-to-substrate tensile creep behavior of an as-deposited 2473 K (2200°C), substrate-nucleated, pyrolytic carbon was investigated over the temperature range 2773 to 3173 K (2500-2900°C) and the stress range  $34.5 - 207 \times 10^6 \text{ N/m}^2$  (5000-30,000 psi) under deadweight loading. A stress-change technique was combined with a graphical-interpolation analysis to obtain data on the stress  $\sigma$  and temperature  $T$  dependence of the creep rate  $\dot{\epsilon}$  over broad strain  $\epsilon$  and stress or temperature ranges on individual specimens. These data were used to determine the stress exponent  $n$  and the activation energy  $\Delta H$  in the empirical expression  $\dot{\epsilon} = A \delta^n \exp(-\Delta H/RT)$ .

Two distinct deformation regimes were confirmed. After 1-2% gage elongation, an increase in  $\epsilon$  indicated a change in deformation mechanism. In the same range,  $n$  dropped from an initial value of  $\sim 4$  to  $1.5 \pm 0.4$ , where it remained to at least 30% elongation independent of  $T$  and  $\delta$ . In agreement with other results on deformation and graphitization of

graphitizing carbons and graphite,  $\Delta H = 250 + 40 \text{ kcal/mole}$ .

During the first 8% elongation, several changes occurred in structure and properties. A density increase of  $\sim 2\%$  and a large increase in Young's modulus were produced by the graphitization and preferred orientation increase (reported elsewhere) that occur in this range. The reduction in area showed that, aside from the graphitization volume decrease, the deformation occurred at constant volume to at least 30% elongation. After the early anomaly,  $\dot{\epsilon}$  decreased regularly with increasing  $\epsilon$ . Creep recovery was small, and appeared to decrease with increasing preferred orientation.

The first stage of deformation was dominated by breakdown of the as-deposited structure, evidently involving dislocation glide and climb. Among various mechanisms considered for the second-stage deformation, which occurs in highly-oriented, well-graphitized material, self-diffusion mass transport was most consistent with the observations.

The following documentation may be obtained from:

National Technical Information Service  
Springfield, Virginia 22151  
Single document price \$6.00  
(or microfiche \$0.95)

### Reference:

NASA-CR-103846 (N69-33446), Tensile Creep-Rate Studies on Pyrolytic Carbon

Source: D. B. Fischback of  
Caltech/JPL  
under contract to  
NASA Pasadena Office  
(NPO-11254)

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## POLYMERIZATION OF PERFLUOROBUTADIENE

A new polymer form of perfluorobutadiene and a new method of production have been developed. Previous methods required extremely high pressures, on the order of  $10^4$  atmospheres, which placed severe limitations on the equipment, besides increasing hazards and production costs.

The polyperfluorobutadiene obtained by this method has good chemical resistance and can be used where hard elastomers are required. It can also serve as a prepolymer to form high molecular weight material with excellent temperature and other properties.

In the new method, diisopropyl peroxydicarbonate is used as a catalyst to initiate the polymerization of polyperfluorobutadiene. The peroxydicarbonate is dissolved directly in the liquid perfluorobutadiene and the reaction conducted in a sealed vessel at the autogenous pressure of polymerization. The reaction temperature, the ratio of catalyst to monomer, and the amount of agitation determine the degree of polymerization and product yield. With increased temperature (up to about 50°C) or amount of catalyst, the molecular weight of the polymer tends to decrease, while the yield tends to increase.

Analysis of the polyperfluorobutadiene indicates that it is a copolymer of perfluoro-1, 2-and 1,4-butadiene. It has the advantage of two types of double bonds (terminal and internal) which are easily susceptible to cross-linking reactions and graft copolymerizations.

One advantage of diisopropyl peroxydicarbonate

as a catalyst is that it is miscible with the perfluorobutadiene monomer. At least 0.10 weight percent of the catalyst is needed to obtain polymerization. Because it decomposes at 5°C, the solid catalyst is placed into a precooled pressure vessel which is attached to a vacuum line and evacuated. The vessel is further cooled in a liquid nitrogen or dry-ice/acetone bath and perfluorobutadiene is condensed into it. The vessel is then sealed and the materials mixed continuously during the reaction period, which can last from 24 hours to several weeks.

Source: M. Troy and J. Newman of  
McDonnell Douglas Corp.  
under contract to  
NASA Pasadena Office  
(NPO-10863)

*Circle 11 on Reader Service Card.*

## POLYIMIDE POLYMERS PROVIDE IMPROVED ABLATIVE MATERIALS

Continuing research has been directed towards improving the capability of ablative materials to withstand more severe engine combustion environments. Results from this research indicate that these materials have application in supersonic aircraft structures, circuit boards, and adhesive formulation.

Silica-reinforced plastic ablative materials have been studied recently, and it has been shown that the principal heat absorption occurs from the in-depth reaction of silica with carbon to form silicon monoxide and carbon monoxide, e.g.,  $\text{SiO}_2 + \text{C} \rightarrow \text{SiO} + \text{CO}$  (heat absorbed is 2.06 K cal/gm of reactants). Thus, the higher the degree of completion of this highly endothermic chemical reaction per unit weight, the higher the capacity of the ablative material to absorb heat.

Current silica-reinforced plastic ablative materials are formulated from phenolic resins. The resultant ablative composite contains approximately 30% resin, which, during ablative pyrolysis, yields about 50% conversion to char (15% char absolute). By substituting a higher-charring resin for the conventional phenolic resin, the ablative capacity of the resultant composite material can be enhanced.

Polyimide polymers are such high-char resin systems. During pyrolysis, these polymers convert to about 80 weight percent char. By preparing a composite material composed of 20% polyimide resin, the product obtained after pyrolysis consists of 16% char. The 16% char (carbon) and 80% silica represent equal molar quantities and result in more reactants being available for the  $\text{SiO}_2\text{-C}$  endothermic reaction. Consequently, this polyimide ablative composite has a significantly higher capacity to absorb heat.

Theoretical ablative reaction capacity for any resin-silica system is not totally achieved because of kinetic limitations. A solid state reaction is involved and the carbon and silica must diffuse together to provide contact of unreacted materials as the reaction proceeds. Silica is present in glass fiber form and probably never comes in total contact with the available carbon in the system. Therefore, by using finer diameter silica filaments, which provide considerably more surface area per unit volume, the silica-carbon reaction is significantly improved. It is not advised that powdered silica be used because it would be blown from the ablator combustion gas

interface. Thus, the finer diameter silica fiber is recommended.

The new polyimide polymers, their properties and other applications, are described in NASA Tech Brief 69-10118.

Further information is contained in the following documentation:

**Reference:**

Ablative Mechanisms in Plastics with Inorganic Reinforcement by N. Beecher and R.E. Rosensweig, AMERICAN ROCKET SOCIETY JOURNAL, April 1961, pp. 532-539.

Documentation is also available from:

National Technical Information Service  
Springfield, Virginia 22151  
Single document price \$3.00  
(or microfiche \$0.95)

**Reference:**

NASA CR-72460 (N70-19965), Investigation of Resin Systems for Improved Ablative Materials

Source: E. Burns, J. Jones, and H. Lubowitz of TRW Systems Group under contract to Lewis Research Center (LEW-10861)

*Circle 12 on Reader Service Card.*

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## DIFUNCTIONAL POLYISOBUTYLENE PREPARED BY POLYMERIZATION OF MONOMERS ON MOLECULAR SIEVE CATALYST

A process has been devised for producing difunctional polyisobutylene by polymerization of the isobutylene monomer on a molecular sieve catalyst. The new polymer is difunctional in that it has a double bond (unsaturated group) at each end of the hydrocarbon chain. The process is relatively simple and can be easily controlled to yield difunctional isobutylene polymers (or prepolymers) ranging in molecular weight from 1150 to 3600. These polymers show a potential for copolymerization and cross-linking with other monomers to form new and useful elastomeric materials.

Experimental quantities of the difunctional polyisobutylenes were prepared in a 300 ml flask equipped with a magnetic stirrer and a side filling tube which could be sealed to a vacuum manifold. In beginning a run, a weighed amount of molecular sieve granules having 5 Å pores is placed in the flask and the system is degassed under vacuum ( $10^{-4}$  to  $10^{-6}$  torr), with intermittent heating to 100°C. The flask is then placed in a liquid nitrogen bath and a measured volume of reagent grade isobutylene is condensed onto the molecular sieve. The contents of the flask are degassed at  $10^{-6}$  torr, quickly warmed to reaction

temperature (at which isobutylene is liquid), and finally stirred at autogenous pressure for a given period. After distillation of excess isobutylene and other low-boiling fractions from the flask, the molecular sieve is washed with pentane to dissolve the adsorbed polyisobutylene. The resultant solution is washed with water in a separatory funnel and dried over anhydrous magnesium sulfate. The solution is then decanted from the drying agent and evaporated at reduced pressure until the polymer appears. It is recovered as a clear, colorless, viscous liquid after final vacuum drying at 50°C. The molecular weight and percentage yield of the polyisobutylene were found to increase as the reaction period (contact time on the molecular sieve) increased or the temperature increased over the range from -141° to +35°C.

Source: J. A. Miller, Jr. of Caltech/JPL under contract to NASA Pasadena Office (NPO-10893)

*Circle 13 on Reader Service Card.*

## NEW HYPERTHERMAL THERMOSETTING HETEROCYCLIC POLYMERS

Polyimidazopyrrolone ("Pyrrone") polymers are formed by the condensation reaction of aromatic dianhydrides with aromatic tetraamines in various solvents and are excellent thermosetting resins that form moldings resisting degradation in air and retaining great strength at temperatures between 477 and 644 K (400° and 700°F). Varnishes made from the resins can be used to manufacture reinforced moldings or laminates. The resins have good insulating properties, are easy to mold, and make good protective coatings.

One such resin was prepared by addition of 3,3', 4,4'-benzophenonetetracarboxylic dianhydride (96.6 g, 0.3 mole) to 500 ml of hot absolute ethanol. Upon the drop-by-drop addition of 20 ml of concentrated sulfuric acid, the dianhydride dissolved. After the reaction mixture was stirred at reflux for 20 hours, ethanol was distilled until the temperature of the mixture rose above 100°C. Dissolved in ether, the residue was washed several times with water; it was then shaken with a 10% solution of sodium bicarbonate until acidification of the bicarbonate washes failed to produce a precipitate. After drying over anhydrous magnesium sulfate, the ether was evaporated and a product weighing 89.3 g (0.19 mole) was collected — 63% of the theoretical product.

This product was dissolved in 500 ml of absolute ethanol, and 3,3'-diaminobenzidine (40.5 g, 0.19 mole) was added to the refluxing solution. Ethanol was distilled from the resultant slurry until the

temperature rose to 150°C at which point the mixture became a viscous melt. While being stirred the mixture was heated further to about 200°C; after 90 minutes, it became too viscous for stirring. When cooled, the melt became a brittle glass, weighing 108.4 g, that could be ground and used as a molding powder. When dissolved in N,N-dimethylacetamide, the partially reacted product served as a varnish. Fiberglass laminates had flexural strengths exceeding  $4.8 \times 10^8$  N/m<sup>2</sup> (70,000 psi), and moduli exceeding  $207 \times 10^8$  N/m<sup>2</sup> (3,000,000 psi) were readily achieved.

Title to this invention has been waived under the provisions of the National Aeronautics and Space Act [42 U.S.C., 2457 (f)], to Hughes Aircraft Co., Culver City, California 90230.

The following documentation may be obtained from:

National Technical Information Service  
Springfield, Virginia 22151  
Single document price \$6.00  
(or microfiche \$0.95)

### Reference:

NASA-CR-1310 (N69-26448). Development and Processing of Pyrrone Polymers

Source: N. Bilow, A. L. Landis, and  
L. J. Miller of  
Hughes Aircraft Co.  
under contract to  
Langley Research Center  
(LAR-10221)

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## PROCESS FOR SYNTHESIZING A NEW SERIES OF FLUOROCARBON POLYMERS

A laboratory process has been devised for the preparation of a new series of fluorocarbon polymers. The resulting products include resins having elastomeric properties at ambient and cryogenic temperatures down to 77 K (−196°C), and rigid or semi-rigid resins that are resistant to oxidizing acids and solvents which attack conventional fluorocarbon polymers.

In general, the new fluorocarbon materials are prepared under carefully controlled conditions in a two-step reaction involving a polyperfluoropolyene (typified by polyperfluorobutadiene), fluorine, and any monomer that can undergo free-radical polymerization (typically highly fluorinated compounds such as tetrafluoroethene and perfluorobutadiene). In the first step, gaseous fluorine is added to the

selected polyperfluoropolyene to create fluorocarbon radicals, with reactive sites at the unsaturated carbon atoms on the polymer chains. In the second step, the monomer is introduced, after evacuation of the fluorine gas from the reaction vessel, and allowed to copolymerize with the free radicals formed in the first step for a specified time.

Source: M. S. Toy of  
McDonnell Douglas Corp.  
under contract to  
NASA Pasadena Office  
(NPO-10862)

*Circle 14 on Reader Service Card.*

## SOLUBLE, HIGH MOLECULAR WEIGHT POLYIMIDE RESINS

Continuing research on new polyimide resins is being directed towards improving processing capabilities as well as physical and chemical properties. Recent work has produced a new class of high molecular weight polyimide resins which have greater than 20% (by weight) solubility in polar organic solvents. Thus, these polyimides permit fabrication into films, fibers, coatings, reinforced composite, and adhesive product forms. Other outstanding characteristics include good thermo-oxidative stability up to 589 K (600°F), and excellent mechanical properties, such as toughness, flexibility, and high modulus. Having relatively straightforward preparation and fabrication characteristics, and stable shelf life in solid or varnish form, these soluble high molecular weight polyimide resins could be used in many industrial applications.

Because of solubility limitations of currently available fully cured polyimide resins, they are usually marketed in an amic-acid precursor form. Processing is difficult, however, because the precursor is thermally and hydrolytically unstable, and for condensation cure reactions, volatile material is released when chemically advancing the precursor to the polyimide form.

The new polyimides are prepared from a new dianhydride monomer, and aromatic and aliphatic diamines and diisocyanates. One new polyimide is prepared by reacting appropriate quantities of the ingredients in common organic solvents, such as dimethyl formamide. The fully imidized high molecular weight resins can be separated for ease in storage. At a later date they can be redissolved in common organic polar solvents to greater than 20% w/w solubility, to form varnishes for use in preparing cast polyimide films, fibers, coatings, or reinforced composite products.

The characterization properties for one typical soluble polyimide resin composition are listed in the Table.

Characterization Test	Test Results
1. Inherent viscosity* (in 0.5% dimethyl formamide)	0.4 deciliters per gram
2. Molecular weight	20,000
3. Thermal stability	300°C
4. Isothermal weight loss in air at 589 K (170 hours)	8%
5. Tensile strength	69 x 10 <sup>6</sup> N/m <sup>2</sup> (10,000 psi)
6. Elongation	10%
7. Initial modulus (determined on 1-mil-thick film samples by triplicate Instron breaks)	207 x 10 <sup>7</sup> N/m <sup>2</sup> (300,000 psi)
8. Solubility	20% polymer in: Dimethyl formamide, Dimethyl sulfoxide, Hexamethyl phosphoramide, Chloroform
9. Film appearance (by sight)	Clear
10. Film appearance (by touch)	Tough, creasable
*Capability of polymer to increase viscosity of solvent — natural logarithm of relative viscosity per concentration.	

Title to this invention has been waived under the provisions of the National Aeronautics and Space Act [42 U.S.C. 2457 (f)] to TRW Systems Group, One Space Park, Redondo Beach, California 90278. (Attn: Mr. Ernest R. Boller)

Source: H. R. Lubowitz and R. J. Jones of  
TRW Systems Group  
under contract to  
Lewis Research Center  
(LEW-11056)

## FILLED POLYMERS FOR BEARINGS AND SEALS USED IN LIQUID HYDROGEN

The use of fillers has resulted in reduced wear rate and improved mechanical properties (compressive modulus and shear strength) of polymers for use in liquid hydrogen. The best results were obtained with compositions containing 60% graphite and 40% nylon; 15%  $\text{Al}_2\text{O}_3$  and 85% PTFCE (polytrifluorochloroethylene); and 15 and 25% glass fiber in PTFCE.

The relatively poor lubricating properties of liquid hydrogen require that surfaces in sliding contact in the presence of liquid hydrogen be self-lubricating. The bearings and seals of liquid-hydrogen turbopumps require materials that will operate for long periods of time under severe conditions of load and speed. PTFE (polytetrafluoroethylene), as a base material, has been used with success for bearing and seal materials in liquid hydrogen. PTFE, however, tends to exhibit cold flow under pressure, and also has a large coefficient of thermal contraction. To minimize these undesirable characteristics, new material combinations were needed.

Friction and wear experiments were performed on nine selected polymers with various fillers, to determine: (1) whether the polymer materials had good lubricating properties; (2) whether they had mechanical properties better than PTFE for sliding contact in liquid hydrogen; and (3) the effect of fillers on these properties. The results of the tests were compared

with a reference material, filled PTFE (80% PTFE + 15% glass fiber + 5% graphite).

Friction of most of the polymers was similar to that of the PTFE. A comparison of the physical properties of four of the PTFCE's (those filled with 15 and 25% graphite, and with 15 and 25% glass fiber) with the reference material, showed that the filled PTFCE's have higher compressive moduli (factors of 4 to 7), and lower coefficients of thermal contraction (factors from one-fourth to two-thirds).

Although the filled polymers tested did not have lower friction or wear, they all showed better thermal stability, less creep, and higher compressive moduli than filled PTFE.

The following documentation may be obtained from:

National Technical Information Service  
Springfield, Virginia 22151  
Single document price \$6.00  
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### Reference:

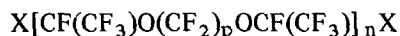
NASA-TN-D-5073 (N69-19800), Friction and Wear of Nine Selected Polymers with Various Fillers in Liquid Hydrogen

Source: D. W. Wisander and R. L. Johnson  
Lewis Research Center  
(LEW-10887)

## PREPARATION OF PERFLUOROPOLYETHER PREPOLYMERS

A new group of fluorinated prepolymers can be used to generate a wide variety of highly fluorinated polymers. The polymers possess most of the desirable properties of polytetrafluoroethylene, such as non-flammability and high corrosion resistance, while retaining good low temperature flexibility.

The prepolymers have the general formula:



Where  $n$  is an integer from 2 to 12

$p$  is an integer from 2 to 23 and

$\text{X}$  is an organic group, either the acid fluoride  $-\text{COF}$  or the methanol group  $-\text{CH}_2\text{OH}$ .

The prepolymers are derived by subjecting a diacid fluoride perfluoroether (the above formula with  $n = 1$  and  $\text{X} = -\text{COF}$ ) to ultraviolet irradiation. By a process of photochemical coupling, molecules bearing the acid fluoride termination are created with the value  $n$  ranging from 2 to 12. The predominant value of  $n$  in the product may be controlled by varying either the intensity and wavelength of the UV or the exposure time. Satisfactory prepolymers with  $n$  ranging from 2 to 4 (molecular weight approximately 1200 to 2300), have been obtained through irradiation for four days with a 450 W UV source.

To obtain hydroxy-terminated (diol) compounds, which are even more useful as prepolymers, the acid

fluoride-terminated form is reduced by reaction with either lithium-aluminum hydride or sodium borohydride. The prepolymer is dissolved in a solvent such as Freon 113, and the solution is added to the reducing agent dissolved in diethylene glycol dimethyl ether. The reaction is performed under anhydrous conditions to prevent hydrolysis of the acid fluoride group.

Information on a continuation of this work, involving the use of the perfluoropolyether prepolymers

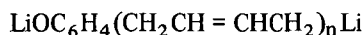
to form fluorinated polyurethanes, may be found in NASA Tech Brief B71-10005. Other related information is contained in NASA Tech Brief B70-10353.

Source: E. C. Stump, Jr., and S. E. Rochow of  
Peninsular ChemResearch Inc.  
under contract to  
NASA Pasadena Office  
(NPO-10765)

*Circle 15 on Reader Service Card.*

### POLYMER CONTAINING FUNCTIONAL END GROUPS IS BASE FOR NEW POLYMERS

Butadiene has been polymerized with lithium-p-lithiophenoxide (lithium salt of p-hydroxyphenyl lithium) to produce a linear polymer containing an oxy-lithium group at one end and an active carbon-lithium group at the other end. This polybutadiene-based polymer



is one of a class of macromolecules that have been designated "living polymers." Such polymers will remain stable even after long storage periods, and will still be capable of reacting with specific monomers to form more complex polymers.

These living polymers represent a new approach to the preparation of difunctional polymers in which structural features, molecular weight, type, and number of end groups can be controlled. For example, the polybutadiene-based living polymer has been reacted with silicon tetrachloride to form a four-

armed star polymer centered on the silicon atom and terminated at each arm by a lithiophenoxide group. The living polymer has also been reacted with carbon dioxide to produce a polymer terminated at one end with a phenolic hydroxyl group and at the other with a carboxyl group. The latter polymer molecule can be reacted at either end or at both ends to form star, block, and graft polymers. These new polymers have potential application in the development of binders, adhesives, elastomers, protective coatings, and structural materials where specific chemical and physical requirements must be met.

Source: S. M. Hirschfield of  
North American Rockwell Corp.  
under contract to  
NASA Pasadena Office  
(NPO-10998 & 10999)

*Circle 16 on Reader Service Card.*

### POLYMERIZATION OF PERFLUOROBUTADIENE AT NEAR-AMBIENT CONDITIONS

Perfluorobutadiene may be homopolymerized to new linear perfluoropolyenes and vulcanizable fluoroelastomers through the use of a peroxide catalyst under mild conditions. The resulting polyperfluorobutadiene is useful as a hard elastomer for seals and other applications where good chemical resistance is needed. The material can also serve as an intermedi-

ate in graft polymerizations and can be cross-linked to provide high molecular weight materials.

A peroxide catalyst is mixed with the monomer material to cause the desired polymerization. The catalyst and monomer are placed in a vacuum sealed flask, and the polymerization is permitted to proceed at autogenous pressure. The temperature can range

from ambient to 393 K (120°C). One catalyst, di-*t*erbutyl peroxide, yields a low molecular weight material. Another peroxide, bis-(trifluoromethyl) peroxide, yields a higher molecular weight product and gives a much greater yield. Almost qualitative yields of up to 95% are obtainable using the latter catalyst and ultraviolet light.

Source: M. S. Toy of  
McDonnell Douglas Corp.  
under contract to  
NASA Pasadena Office  
(NPO-10447)

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### COATINGS FROM COPOLYMERS OF TETRAPHENOXYSI- LANE AND P,P'-BIPHENOL

Heat-resistant coatings have been prepared by melt-condensing tetraphenoxysilane with p,p'-biphenol. The resultant resin is highly crosslinked and completely aromatic. The procedure used includes developing the polyaryloxysilane structure "in situ" after the substrate has first been coated with a prepolymer.

The subject resins are potentially useful as protective coatings for metals, ceramics, glass, and other materials that can accommodate relatively high curing temperatures. In their partially polymerized forms, they could also be useful as modifier resins, such as phenolics, which are used in laminating and molding applications where high temperatures and pressures are involved.

A series of three-dimensional polyaryloxysilane structures has been prepared by crosslinking low molecular weight phenolic OH-terminated polymers with tetra- or tri-phenoxysilanes. Several of these

cured polymers exhibited good coating properties but underwent moderate material losses with prolonged exposure in air at 523 K (250°C).

The following documentation may be obtained from:

National Technical Information Service  
Springfield, Virginia 22151  
Single document price \$6.00  
(or microfiche \$0.95)

#### Reference:

NASA-CR-85820 (N67-31379), Process Development and Pilot-Plant Production of Silane Polymers of Diols

Source: R. A. Market and W. R. Dunnivant of  
Battelle Memorial Institute  
under contract to  
Marshall Space Flight Center  
(MFS-14947)

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### POLYIMIDE POLYMERS PROVIDE HIGHER CHAR YIELD FOR GRAPHITIC STRUCTURES

Composite Materials consisting of graphite fiber-reinforced graphitic matrices (pyrolyzed plastics) are currently being investigated for a wide range of high temperature applications. These composite materials can be used in ablative materials, supersonic aircraft structures, jet engine components, circuit boards, and flexible electrical cable insulation.

Conventionally, the manufacture of these graphitic composites requires many processing steps resulting in expensive end products. In an effort to reduce both cost and processing complexity, a technique has been developed that uses new, high-char-

forming processable polyimide resin systems, to produce the graphitic matrix.

Current processes employ phenolic resin matrix systems which yield about 40 to 60% of graphitic residue on pyrolysis. The operation consists of first preparing a graphite fiber-reinforced resin, pyrolyzing it under controlled environment, reimpregnating the charred product with phenolic resin, and finally repyrolysis. The series of steps is repeated in a cyclic fashion and then followed by repetitive graphitic deposition from low molecular weight gases to build up the total graphitic yield to acceptable



values (e.g., 99.7% balance voids). Typically, seven cyclic impregnation and pyrolysis steps are required using phenolic resins to yield a 99.7% graphite product. The many repetitive steps required in this process are time consuming and costly.

The new polyimide resin systems pyrolyze to a product having 75 to 90% graphitic residue, and also evolve a lesser quantity of gaseous by-products. Only three cyclic steps are required using the new resin systems to yield a 99.7% graphite product. Fabrication techniques are standard, but the number of repetitive processing steps is minimized.

The new polyimide polymers, their properties, and other applications, are described in NASA Tech Brief 69-10118.

The following documentation is available from:  
National Technical Information Service  
Springfield, Virginia 22151  
Single document price \$3.00  
(or microfiche \$0.95)

Reference:

NASA-CR-72460 (N70-19965), Investigation of  
Resin Systems for Improved Ablative Materials

Source: E. A. Burns, J. F. Jones, and

H. R. Lubowitz of

TRW Systems Group

under contract to

Lewis Research Center

(LEW-10860)



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— NATIONAL AERONAUTICS AND SPACE ACT OF 1958

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